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(71) Applicant: **DYNEON LLC** [US/US]; 6744 33rd Street
North, Oakdale, MN 55128 (US).

(72) Inventors: **BLAEDEL, Hermann**; Post Office Box
33427, Saint Paul, MN 55133-3427 (US). **BRIERS, Joris**;
Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agent: **LILLY, James V.**; Office of Intellectual Property
Counsel, Post Office Box 33427, Saint Paul, MN 55133-
3427 (US).

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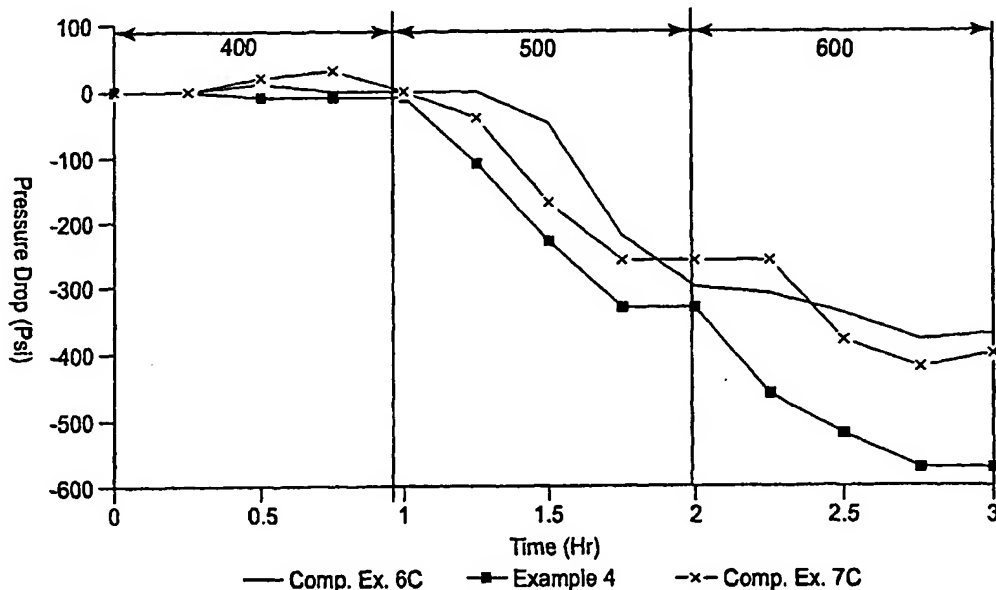
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(54) Title: PROCESS AID FOR MELT PROCESSABLE POLYMERS



(57) Abstract: A fluorine-containing process additive with improved flow properties. The process additive also provides thermo-
plastic compositions with improved extrusion performance characteristics and comprises a latex blend of simultaneously coagulated
fluoropolymer components.

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PROCESS AID FOR MELT PROCESSABLE POLYMERS

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FIELD OF THE INVENTION:

The present invention relates to fluoropolymer processing aids, their preparation and use, and shaped articles made using such processing aids.

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BACKGROUND OF THE INVENTION:

The melt extrusion of high molecular weight polymers into shaped structures such as tubing, pipe, wire coating or film is accomplished by well-known procedures. For example, a rotating screw pushes a heated, molten and viscous polymer melt through the extruder barrel into a die in which the polymer is shaped to the desired form. The shaped polymer is then subsequently cooled and resolidified, by various means, into the general shape of the die.

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In order to achieve low production costs it is desirable to extrude at high rates. Although the extrusion rate is readily increased by increasing the rate of revolution of the extruder screw, there are technical limits to these increases because of the viscoelastic properties of the polymer. Under certain conditions, adding energy to the polymer mechanically may raise melt temperatures to a range at which thermal decomposition can occur. If polymer shear rate limits are exceeded, shaped articles may contain surface defects. Such surface defects are also known as melt fracture, "orange peel" or "sharkskin." One way of avoiding such surface defects is to extrude at a higher temperature, but this adds to the processing costs and makes cooling of the extrudate more difficult. More seriously, many polymers are already extruded at temperatures near their decomposition temperature, and further increases are not feasible. Increases in operating pressure may also be used to increase output. Such pressure increases also have practical limitations due to equipment design, safety considerations and the effect this change has on shear rate of the polymer.

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Die build-up or die drool is another category of processing defect. Die drool is generally described as build-up of the polymer at the orifice of the die. This results in a slowing of the extrusion process either because the process must be stopped to clean the

equipment or because the process must be run at a slower speed to minimize the problem. Die build-up is a problem with non-olefinic polymers, e.g. polyamides or PVC. Thus, while these polymers may not exhibit surface defects, there are still problems encountered at high extrusion rates.

5 It is desirable, therefore, to find a highly efficient means of increasing the extrusion rate, without raising the melt temperature, while producing products with smooth surfaces and minimum die build-up. Changes in extruder and die configuration can improve melt flow but are not always practical or economically feasible. Another way to improve extrusion rate involves the addition of conventional wax-type process aids which reduce
10 bulk viscosity and in some cases improve processing properties. However, the efficiency is marginal and the high levels of additive required often adversely affect other properties. Yet another approach is disclosed in Blatz, U.S. Pat. No. 3,125,547. This patent discloses that melt extrudable hydrocarbon polymers that contain from 0.01-2.0 % of a fluorocarbon and that have a melt flow behavior similar to that of the hydrocarbon polymer, improve
15 the extrusion characteristics of the hydrocarbon polymer.

 Combinations of fluorocarbon polymers with other materials, including other fluoropolymers, are also known, see for example, Duchesne, Johnson, U.S. Pat. No. 4,855,360 and Chapman, Priester U.S. Pat. No. 4,904,735. The use of a fluoroelastomer latex or aqueous fluoropolymer dispersion as a process aid is also known, see for example,
20 Priester, WO 98/30619.

 A problem which may be encountered when using fluoroelastomer or amorphous or low melting fluoropolymer processing aids is the lack of a free-flowing nature of such materials. This may lead to problems in handling or processing. Many such process aids have a tendency to compact, i.e., to clump or cake together, during storage or use. This
25 compaction problem has been addressed by adding partitioning agents, such as barium sulphate, silica, calcium stearate or polyolefin powder, to the fluoroelastomer or amorphous fluoropolymer process aid. See for example, Arcella et al, U.S. Pat. No. 4,746,573. Such partitioning agents may minimize the compaction or sticking problem, but may add a contaminate to the final composition. They also generally require an extra
30 processing step to add the partitioning agent to the process aid.

 A need still exists for a solution to the compaction problem without the addition of a partitioning agent. A need also exists to provide a processing aid that has improved

performance. Such improved performance may be characterized either by increased pressure drop during the extrusion process; by greater reduction in the apparent viscosity of the extruded composition; by an increase in the throughput rate of the polymer; by elimination of die drool; or by some combination of the above.

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SUMMARY OF THE INVENTION

The present invention provides, in one embodiment, a co-coagulated fluorine-containing polymer composition useful as a processing additive in the extrusion of difficultly melt processable polymer (i.e., a host polymer). The fluorine-containing polymer composition of the invention comprises the co-coagulated product of

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- a) a first fluoropolymer component selected from an amorphous fluoropolymer, a semi-crystalline fluoropolymer, or blends thereof, and
- b) a second fluoropolymer component comprising a semi-crystalline fluoropolymer.

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Another embodiment of the invention provides granules of agglomerated particles wherein each granule comprises

- a) a first fluoropolymer component selected from an amorphous fluoropolymer, a semi-crystalline fluoropolymer, or blends thereof, and
- b) a second fluoropolymer component comprising a semi-crystalline fluoropolymer.

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In one preferred aspect of these embodiments, the first and second fluoropolymer components are each semi-crystalline and the melt point of the first component is below the melt point of the second component. When this composition is employed as a processing additive in a host polymer, it is highly preferred that the processing temperature of the host polymer be between the melt points of the first and second fluoropolymer components.

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In a second preferred aspect of these embodiments, the first and second fluoropolymer components are each semi-crystalline and the melt point of the first component is below that of the second component and is less than 150° C.

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In a third preferred aspect of these embodiments, the first and second fluoropolymer components are each semi-crystalline and the melt point of the second component is at least 10° C higher than the melt point of the first component.

In another preferred aspect of the invention, the first fluoropolymer component comprises an amorphous fluoropolymer.

The present invention also provides a method for improving the performance of the extrusion of a host polymer comprising the steps of,

- 5 a. providing a coagulum of a simultaneously coagulated blend of latex particles comprising a first fluoropolymer component comprising (i) an amorphous fluoropolymer, (ii) a semicrystalline fluoropolymer, or (iii) a blend thereof, and a second fluoropolymer component comprising a semicrystalline fluoropolymer, and
- 10 b. combining an effective amount of the coagulum with the host polymer, and
- c. extruding the combined product of step b.

A further aspect of this invention relates to a method for providing a fluorine-containing polymer process aid with improved flow properties comprising the steps of,

- 15 a. providing a first latex component comprising an amorphous fluoropolymer, a semi-crystalline fluoropolymer or blends thereof,
- b. providing a second latex component comprising a semi-crystalline fluoropolymer,
- c. blending the first and second latex components to form a latex blend,
- d. simultaneously coagulating the latex blend to form a coagulum,
- 20 e. separating the coagulum from the liquid of the latex blend, and
- f. optionally, reducing the particle size of the coagulum.

In one preferred aspect of these embodiments, the first and second latex components comprise fluoropolymers that are each semi-crystalline and the melt point of the fluoropolymer in the first component is below the melt point of the fluoropolymer in the second component. When combined with a host polymer, it is highly preferred that the processing temperature of the host polymer be between the melt point of the fluoropolymer in the first component and the melt point of the fluoropolymer in the second component.

In a second preferred aspect of these embodiments, the first and second latex components comprise fluoropolymers that are each semi-crystalline and the melt point of the fluoropolymer in the first component is below that of the second component and is less than 150° C.

In a third preferred aspect of these embodiments, the fluoropolymers comprising the first and second latex components comprise fluoropolymers that are each semi-crystalline and the melt point of the fluoropolymer in the second component is at least 10°C higher than the melt point of the fluoropolymer in the first component.

5 In another preferred aspect of the invention, the first latex component comprises an amorphous fluoropolymer.

Still further aspects of this invention relate to an extrudable composition comprising the difficultly melt-processible polymer and an effective amount of the fluorine-containing process aid made according to this invention, and to shaped articles
10 made therefrom.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows curves of apparent viscosity versus apparent shear rate generated by a capillary Rheometer for polymer compositions described in Examples 1 and 2 and
15 Comparative Examples 1C and 2C. Figures 2 and 3 show % Melt Fracture and Pressure Drop respectively, versus time and additive concentration for blown films made as described in Example 4 and Comparative Examples 6C and 7C.

DETAILED DESCRIPTION

20 The present invention provides a fluorine-containing process aid which, when combined with a difficult-to-process host polymer, shows improved extrusion characteristics. This comparison is with process aids with similar compositions made by other methods. Such host polymers may also be referred to as difficultly melt-processible polymers. The improved extrusion characteristics obtainable are in addition to the
25 reduction or substantial elimination of surface defects and/or die build-up. The improvements over other fluorinated process aids of similar composition include: higher pressure drop through the extrusion process equipment, lower apparent viscosity during the extrusion, higher throughput of extrudate at equivalent pressure drop, reduced die build-up or a combination of the above tailored for specific circumstances. The higher
30 pressure drop translates to a lower pressure at the die for similar extrusion conditions.

The fluorine-containing process aid of this invention comprises two components. The first component comprises an amorphous fluoropolymer, a semi-crystalline

fluoropolymer or blends thereof and the second component comprises a semi-crystalline fluoropolymer. The method of the invention comprises simultaneous coagulation or co-coagulation of the two components in latex form to produce a blend of the components. The resulting co-coagulated blend of fluoropolymers may then be combined with the
5 difficultly melt-processible polymer.

When both the fluoropolymer of the first component and the fluoropolymer of the second component are semi-crystalline, the first component is preferably selected such that its melt point is less than the temperature used to process the difficultly melt-processible polymer and the second component is selected such that its melt point is equal
10 to or higher than the processing temperature.

The fluorocarbon or fluorine-containing amorphous polymers useful as a first component in this invention are generally copolymers of fluorinated olefins having a fluorine atom-to-carbon atom ratio of at least 1:2, preferably at least 1:1. Amorphous copolymers of fluorinated olefins can be those derived, for example, from vinylidene
15 fluoride, and one or more additional olefins, which can be fluorinated, e.g. hexafluoropropylene, or non-fluorinated, e.g. propylene.

Preferred amorphous fluorocarbon polymers are copolymers of vinylidene fluoride with at least one terminally unsaturated fluoromonoolefin containing at least one fluorine atom on each double-bonded carbon atom, each carbon atom of said fluoromonoolefin
20 being substituted only with fluorine, chlorine, bromine, hydrogen or lower fluoroalkyl (e.g. perfluoroalkyl having one to four carbon atoms) or fluoroalkoxy radical, (e.g. perfluoroalkoxy having one to four carbon atoms). Preferred comonomers with vinylidene fluoride are perfluoropropylene, tetrafluoroethylene, chlorotrifluoroethylene, and pentafluoropropylene. Particularly preferred are the fluorinated polymers produced by
25 copolymerizing perfluoropropylene and vinylidene fluoride, as described in U.S. Pat. Nos. 3,051,677 (Rexford) and 3,318,854 (Honn, et al.) and those polymers produced by copolymerizing perfluoropropylene, vinylidene fluoride and tetrafluoroethylene as described in U.S. Pat. No. 2,968,649 (Pailthorp et al.). The amorphous copolymers of
30 perfluoropropylene and vinylidene fluoride having between about 15 and about 50 mole percent perfluoropropylene, optionally with the addition of up to 5 to 30 mole percent tetrafluoroethylene, are particularly useful. Such amorphous fluoropolymers are

commonly used in applications requiring cure chemistry to produce a cross-linked fluoropolymer with elastomeric properties.

The semi-crystalline fluoropolymers useful in the first component are those fluoropolymers copolymerized from monomers such as vinylidene fluoride or
5 tetrafluoroethylene with fluoromonomers such as hexafluoropropylene or perfluorinated alkyl vinyl ethers that have the effect of reducing the melt point of the resulting copolymer. Other useful fluorine-containing comonomers include chlorotrifluoroethylene, 1-hydropentafluoropropylene and 2-hydropentafluoropropylene or non-fluorinated monomers, such as, ethylene or propylene. A preferred class of useful first component
10 semi-crystalline fluoropolymers have a melting point less than the processing temperature used in the processing of the difficultly melt-processible polymer. In another embodiment, a useful first fluoropolymer component preferably has a melt point below that of the second component and is less than 150° C.

The semi-crystalline fluoropolymers preferred as the first component
15 fluoropolymer are those fluoropolymers having at least 5 wt % of units derived from vinylidene fluoride and more than 25 wt % of their units derived from a combination of tetrafluoroethylene and hexafluoropropylene such that the fluoropolymers have an amount of fluorine below 75 wt % and are melt-extrudable thermoplastics. Methods to make such fluoropolymers are generally known and include the methods described in U.S. Pat. No.
20 4,335,238 (Moore et al).

Another preferred class of the fluoropolymers used in this invention is derived by copolymerizing 30 to 70 wt %, preferably 35 to 65 wt %, tetrafluoroethylene, 10 to 30 wt %, preferably 15 to 25 wt %, hexafluoropropylene, and 10 to 50 wt %, preferably 15 to 45 wt %, vinylidene fluoride. A subclass of the fluoropolymer useful in making blends of
25 this invention are fluoroplastics which contain interpolymerized units derived from copolymerization of a monomer charge of 45 to 65 wt % tetrafluoroethylene, 10 to 20 wt % hexafluoropropylene, and 20 to 35 wt % vinylidene fluoride. The fluoropolymers of this class, described in U.S. Pat. No. 4,670,503 (Neumann et al.), having melting points of 130° to 170°, measured by Differential Scanning Calorimetry and an ASTM D 1238 melt
30 index of 50 to 250 g/10 min. measured at 265° C. and a loading of 5 kg.

The fluorocarbon polymers useful as a second component in this invention are semi-crystalline in nature. These include homopolymers of tetrafluoroethylene and

copolymers of tetrafluoroethylene with certain copolymerizable monomers. Useful second component fluorocarbon polymers include high molecular weight polymers, whether the fluoropolymer is melt-processible or not melt-processible. The polymer may be made by dispersion polymerization or suspension polymerization. Limitations on how much comonomer or which copolymer may be present are governed primarily by the requirement to maintain a semi-crystalline nature. When used with a semi-crystalline fluoropolymer first component and combined with a host polymer, it is preferable for the second component fluoropolymer to have a melting point equal to or greater than the processing temperature used to process the non-fluorinated thermoplastic polymer or host polymer. Preferred fluoropolymers useful in a second component in this invention are non-melt processible homopolymers or copolymers of tetrafluoroethylene.

The melting point of a second component fluoropolymer will be affected by the amounts and types of comonomer(s) used. When co-coagulated with a fluoropolymer of the first component that is semi-crystalline, the fluoropolymer of the second component is preferably selected such that its melting point is above the melt point of the first fluoropolymer component, more preferably at least 10° C above the melt point of the first fluoropolymer component. In another embodiment, the melt point of the second fluoropolymer component is preferably above the temperature used to process the difficultly melt-processible non-fluorinated polymer. Also, excessive amounts of certain comonomers should be avoided, lest the fluoropolymer of the second component become amorphous. Latex blends of first and second component fluoropolymers that are semi-crystalline may still provide polymer processing improvements. However, the benefits of improving the free flowing nature of such process aids or the need for such improvement may be minimized or eliminated.

Suitable tetrafluoroethylene homopolymers are semi-crystalline and include those that are high molecular weight and fibrillate, or do not fibrillate to a substantial extent under shearing conditions, as well as those which are low molecular weight and non-fibrillating, such as those which have been subjected to ionizing radiation. Suitable monomers copolymerizable with tetrafluoroethylene to give a useful second component fluoropolymer include ethylene, perfluoroolefins such as hexafluoropropylene, and perfluoro(alkyl vinyl ethers), such as perfluoro(propyl vinyl ether). More than one comonomer may be used, provided all the aforesaid requirements are met.

Blending of the first and second fluoropolymer components in this invention takes place in the latex form. It is understood that the discussion above of fluoropolymers for either the first or second component will be in latex or emulsion form prior to blending and co-coagulating of the fluoropolymers. Such latexes will preferably contain, in addition to the fluoropolymer, only such surfactants as necessary to maintain a stable emulsion. In many cases, this will be only the surfactant used during the polymerization process. Any method of blending of the latex dispersions or emulsions is suitable, provided a uniform mixture of the latexes is obtained. The mixing action during blending should avoid the initiation of coagulation of either component before an intimate mixing is accomplished. Paddle mixers, lightning mixers, static mixers or even hand stirring are all examples of suitable mixing devices or processes, as long as they are operated in a manner to provide an intimate mixture and to avoid premature coagulation as mentioned above.

The ratio of the first fluoropolymer component to the second component is based upon the solids present in the respective latexes. A useful range of the solid components for this invention includes co-coagulated compositions comprising from 30% by weight of the first fluoropolymer component to 80% by weight of the first component and correspondingly, 70% by weight of the second component to 20% by weight of the second component. Preferably, a fluorine-containing process aid of this invention will contain 40% to 60% by weight of the first fluoropolymer component. Minor amounts of other materials may be present, provided they do not negatively impact the desired functions of the composition. Such desired functions include elimination of surface defects during extrusion of a host polymer comprising such a process aid, reduction of die pressure, reduction of inherent viscosity, a throughput improvement, a reduction in the level of process aid required, reduction of die build-up or some combination of the above. Preferably, fluorine-containing process aids of this invention will possess a free-flowing nature without the addition of a partitioning agent.

Methods of coagulation of the latex blend include the commonly used coagulation methods. Such methods include thermal coagulation, mechanical shear coagulation, freeze coagulation and chemical coagulation. The specific method selected is not believed critical to the practice of the invention. It is desirable to adequately mix the components prior to initiation of coagulation. The result of this coagulation process is a coagulum of granules comprising particles of both fluoropolymer components.

At the completion of the coagulation process, the fluoropolymer coagulum is separated from the liquid by any suitable means, such as filtration or decantation. The coagulum may then be washed and dried, if required. The resulting coagulum may also optionally be comminuted, i.e., subjected to a size reduction process, such as grinding.

5 Sizing of the granules is generally preferred if they are to be dry blended with another material, such as a host polymer. Providing a processing aid particle size that is similar to the host polymer particle size may tend to minimize the separating or segregating of the dry blended materials that might otherwise occur with subsequent handling.

An additional improvement provided by this invention relates to the handling

10 characteristics of the co-coagulated process aid itself. The preferred fluorine-containing process aid of the invention needs no partitioning agent or anti-caking agent to provide it with a free-flowing property despite comprising a substantial quantity of an amorphous or relatively low melting semi-crystalline fluoropolymer component. Amorphous fluoropolymer process aids discussed in the prior art are commonly dusted or coated with

15 partitioning agents such as barium sulfate, silica, calcium stearate or polyolefin powder. These partitioning agents are provided to counteract the normally tacky nature of the amorphous particles. Without such partitioning agents, the tacky nature of the particles results in sticking or clumping together of the particles. This clumping may be particularly noticeable after long term storage or if the particles are pressed together for

20 any reason. While partitioning agents may reduce the tendency of the particles to clump together, they may also serve to add a foreign material or contaminate to the product. The severity of any problems encountered from such partitioning agents will depend upon, *inter alia*, the amount of partitioning agent present and the chemical similarity of the agent to the host polymer.

25 The improvement in handling is most noticeable when the first fluoropolymer component is amorphous. First component fluoropolymers that are semi-crystalline and have a low melt point also experience an improvement in handling when used in this invention. To realize this improvement, preferably the melt point of the first fluoropolymer component is less than 150° C.

30 The non-fluorinated thermoplastic or melt-processible host polymers that benefit the most from the addition of the fluorine-containing process aids comprise polymers which are generally difficult to melt process. Such difficultly melt-processible polymers

are generally high molecular weight or have low melt flow indexes or both. Such polymers are known to exhibit surface defects when processed at high rates of throughput or under conditions of high shear. Also, certain polymers may exhibit processing problems such as die build-up or die drool. Surface defects are visually objectionable and as such limit the processing range available to the producer. Examples of such non-fluorinated thermoplastic polymers include hydrocarbon polymers, polyamides, chlorinated polyethylenes, polyvinyl chloride and polyesters. Non-fluorinated polymers are defined for the purpose of this invention as those polymers containing a ratio of fluorine atoms to carbon atoms of less than 1:2

Of particular importance are polymers obtained by the homopolymerization or copolymerization of olefins, as well as copolymers of one or more olefins. This includes up to about 30 weight percent, but preferably 20 weight percent or less, of one or more monomers which are copolymerizable with such olefins, e.g. vinyl ester compounds such as vinyl acetate. Said olefins have the general structure $\text{CH}_2=\text{CHR}$, where R is a hydrogen or an alkyl radical, and generally, the alkyl radical contains not more than 10 carbon atoms and preferably one to four carbon atoms. Representative olefins are ethylene, propylene, and butene-1. Representative monomers which are copolymerizable with said olefins are vinyl ester monomers such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl chloroacetate, vinyl chloropropionate, acrylic and alpha-alkyl acrylic acid monomers, and their alkyl esters, amides, and nitriles such as acrylic acid, methacrylic acid, ethacrylic acid, methyl acrylate, ethyl acrylate, N,N-dimethyl acrylamide, methacrylamide, acrylonitrile, vinyl aryl monomers such as styrene, o-methoxystyrene, p-methoxystyrene, and vinyl naphthalene, vinyl and vinylidene halide monomers such as vinyl chloride, vinylidene chloride, vinylidene bromide, alkyl ester monomers of maleic and fumaric acid such as dimethyl maleate, diethyl maleate, vinyl alkyl ether monomers such as vinyl methyl ether, vinyl ethyl ether, vinyl isobutyl ether, 2-chloroethyl vinyl ether, and vinyl pyridine monomers, N-vinyl carbazole monomers, and N-vinyl pyrrolidone monomers. The thermoplastic hydrocarbon polymers also include the metallic salts of said olefin copolymers, or blends thereof, which contain free carboxylic acid groups. Illustrative of the metals which can be used to provide the salts of said carboxylic acid polymers are the one, two and three valence metals such as sodium, lithium, potassium, calcium, magnesium, aluminum, barium, zinc, zirconium, beryllium, iron, nickel and

cobalt. The thermoplastic hydrocarbon polymers also include blends of thermoplastic hydrocarbon polymers with other thermoplastic hydrocarbon polymers or copolymers or blends thereof containing conventional adjuvants such as antioxidants, light stabilizers, fillers, antiblocking agents and pigments. Representative examples of hydrocarbon polymers useful in this invention are polyethylene, polypropylene, polybutene-1, poly(3-methylbutene), poly(4-methylpentene) and copolymers of ethylene with propylene, butene-1, hexene-1, octene-1, decene-1, 4-methyl-1-pentene and octadecene-1.

Representative blends of difficultly melt-processible polymers useful in this invention include blends of polyethylene and polypropylene, low-density polyethylene and high-density polyethylene, and polyethylene and olefin copolymers containing said copolymerizable monomers, some of which are described above, e.g., ethylene and acrylic acid copolymers; ethylene and methyl acrylate copolymers; ethylene and ethyl acrylate copolymers; ethylene and vinyl acetate copolymers; ethylene, acrylic acid, and ethyl acrylate copolymers, and ethylene, acrylic acid, and vinyl acetate copolymers.

The difficultly melt-processible polymers that benefit greatly from the use of this invention are homopolymers of ethylene and propylene and copolymers of ethylene and 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, propylene, vinyl acetate, and methyl acrylate. The difficultly melt-processible polymers may be used in the form of powders, pellets, granules, or any other extrudable form.

The properly sized particles of the fluoropolymer blend may be added to the host polymer by any suitable means. These include dry blending the proper amount of process aid in the host polymer, preparing a masterbatch of the process aid and host polymer for subsequent addition to a process stream comprising a host polymer. The host polymer or carrier polymer of the masterbatch need not be the same as the host polymer to which the masterbatch is added. These host or carrier polymers are preferably the same or at least compatible with each other.

Effective amounts of the fluorine-containing process aid will vary depending on the host polymer and the processing conditions. A first criteria for effectiveness is the ability to substantially eliminate surface defects within a reasonable time after addition of the process aid. The elimination of surface defects may require a time period after addition of the process aid of from several minutes to an hour or more depending on the size of the equipment being used, the quantity of host polymer being processed and the

process conditions selected. A second criteria for effectiveness relates to reduction or elimination of die build-up or die drool during the extrusion process. Some material selection pairs, i.e., host polymer and process aid, may show improvement in one or both of these criteria.

5 Concentrations of from 100 parts per million (ppm) to 5000 ppm of the fluorine-containing process aid in the host polymer are suitable for most purposes. It may be desired to produce a masterbatch of the process aid and a carrier polymer at a higher concentration to facilitate control of the addition rate to the final host polymer. The final
10 concentrations, after letdown, will generally be within the range stated above. A preferred addition range is from 400 ppm to 2000 ppm of the fluorine-containing process aid to the difficultly melt-processible polymer. A more preferred addition range is from 500 ppm to 1200 ppm.

EXAMPLES

15 Samples of process aids and blends of such process aids with olefinic host polymers were made and evaluated using various extension techniques. The evaluations of the samples included determination of an apparent viscosity using a Göttfert Rheotester 1500 capillary rheometer with a 0.5mm die diameter and a 4/1 L/D. The compounds used in the rheometer were prepared by melt mixing in a Haake Rheocord system 90 Meltmixer
20 for 8 minutes at a temperature of 210° C. The batch size prepared for the capillary rheometer tests was 300 g.

 Several samples were evaluated by making blown film samples and measuring a change in pressure during extrusion. The resulting film samples were also evaluated for a reduction or elimination of melt fracture.

25 The host resin used was EXXON LLDPE LLN1201.xv (MI: 0.7 (2.16 kg; g/10min)) unless otherwise specified. All compounds also contain 1000 ppm of Irganox™ 1010 anti-oxidant to ensure a sufficient stabilization of the resin during the test. The different process aids and level of addition that were tested are summarised in Table 1:

 Process aid A was prepared by blending 62.5 parts of a latex of an amorphous
30 fluorine-containing copolymer of 40% by weight HFP and 60% by weight of VF2 and 37.5 parts of a latex of a homopolymer of tetrafluoroethylene (PTFE). In each case, the parts used refers to the quantity of solids of the respective latexes. The latexes were

blended in the latex form using a conventional paddle mixer and mixing for about five minutes. The blended latexes were then co-coagulated using an aqueous solution of MgCl_2 , the resulting crumb or coagulum recovered, washed and dried at 80°C for 5 hours and then 90°C for 20 hours. The dried crumb was then comminuted by grinding to a particle size of 1-3 mm.

Process aid B was prepared in a similar manner except the ratio of solids was 50 parts amorphous fluoropolymer and 50 parts PTFE.

FX5920A and FX9613 are commercial products comprising an amorphous fluoropolymer available from Dyneon LLC, St. Paul, Minnesota. The PTFE used was a low molecular weight emulsion grade PTFE at a latex solids of 20-25%. The only surfactant in the latexes was the perfluorooctanoic acid used during the polymerization process.

Comparative example 3C contained the same two components and the same ratio and additive level as Example 3, but in Example 3 the components were blended in latex form and coagulated together. In Comparative 3C, the components were added separately to the host polymer in the melt mixer.

Table 1

	Example #	Process Aid	Additive level (ppm)
20	1	A	1000
	2	B	1000
	Comparative 1C	FX 5920A	1000
	Comparative 2C	FX 9613	1000
	3	B	600
25	Comparative 3C	FX 9613 + PTFE	300 + 300 (separately added)
	Comparative 4C	FX 9613	600
	Comparative 5C	FX 9613	300

An evaluation of the change in the apparent viscosity resulting from the use of different types of PPA's at a level of 1000 ppm was compared to the control (LLDPE without any process aid) in Figure 1. The testing temperature was 190°C. Examples 1 and 2 and Comparative Example 2C performed in a very similar manner in terms of reduction of apparent viscosity.

Example 3 was compared to Comparative Example 3C in a similar manner. At a shear rate of 100 sec^{-1} , Example 3 and Comparative Example 3C had apparent viscosity

values of 1550 Pas and 1850 Pas respectively. At a shear rate of 200 sec^{-1} , Example 3 and Comparative Example 3C had apparent viscosity values of 850 and 1000 Pas respectively.

Example 3 shows an advantage in a lower apparent viscosity at both of these shear rates, even though comparative Example 3C contains the same components in the same ratio.

The fluorine-containing process aids (the granules of coagulum) resulting from co-coagulating the latexes were observed to have an excellent free flowing nature to them. Conventional amorphous fluoropolymer based process aids are generally tacky or sticky in their raw state and require a partitioning agent be added to provide a free flowing product.

An evaluation on a Kiefel Blown Film line with a 40 mm screw diameter and 24:1 L/D was run using a polyethylene host resin identified as LL 1001.32 (Melt Index 1, density 0.918) available from Exxon. The die diameter was 40 mm and had a gap setting of 0.6 mm, a spiral design with 6 feed ports and a single lip air ring. Masterbatches of three process aids were prepared using LLN 1004.YB, available from EXXON, as a carrier resin.

The masterbatch for Comparative Example 6C was prepared as a 3% concentrate of the process aid used in Comparative Example 2C and for Example 4, a 5% concentrate of the process aid used in Example 2 and the components used in Comparative Example 3C were used to prepare a 5% concentrate for Comparative Example 7C. The ratio of the components used in preparing the masterbatch concentrate for Comparative Example 7C were adjusted for the partitioning agent contained on the amorphous fluoropolymer. This adjustment provided a ratio of 50% amorphous fluoropolymer and 50% PTFE. The partitioning agent was present but not included in the amount of solids attributable to the amorphous fluoropolymer.

The masterbatch addition rate for Comparative Example 6C was adjusted to provide an additive level of 400 ppm and blown film was produced for one hour. Then the addition level was increased to 500 ppm for one hour and more film produced. Then the addition level was increased to 600 ppm and film was made for an additional hour. This sequence resulted in visual melt fracture elimination in the film being produced.

The masterbatch concentrates for Example 4 and Comparative Example 7C were run in a similar manner adjusting the addition rate of the concentrates to provide 400, 500, and 600 ppm of the fluoropolymer process aid. The results of the elimination of melt

fracture are shown in Figure 2. Similar results from all three were obtained. Each sample began to eliminate melt fracture after the addition rate was raised to 500 ppm and essentially complete elimination was achieved shortly after the 600 ppm addition rate was begun. Some variation during the hour at the 500 ppm addition rate was observed, but the
5 elimination of melt fracture was achieved at nearly the same time.

The gate pressure in the extruder was recorded with time. The results are shown in Figure 3. In this test, an advantage of the invention is demonstrated shortly after the addition rate is increased to 500 ppm and continues through the end of the test. The greatest advantage is shown to be a pressure drop increase of about 35%.

10 The process aids evaluated as blown films had similar success in the elimination of visual melt fracture defects as seen in Figure 2. However, the process aid of the invention in Example 4, demonstrated a significant reduction in gate pressure. This is true, even when compared to Comparative Example 7C, containing the same components in the same ratio, but blended in a different manner.

CLAIMS

1. A co-coagulated fluorine-containing process additive comprising the co-coagulated product of
- 5 a) a first fluoropolymer component selected from an amorphous fluoropolymer, a semi-crystalline fluoropolymer, or blends thereof, and
- b) a second fluoropolymer component comprising a semi-crystalline fluoropolymer.
- 10 2. A co-coagulated fluorine-containing process additive comprising granules of agglomerated particles wherein each granule comprises
- a) a first fluoropolymer component selected from an amorphous fluoropolymer, a semi-crystalline fluoropolymer, or blends thereof, and
- b) a second fluoropolymer component comprising a semi-crystalline
- 15 fluoropolymer.
3. A co-coagulated fluorine-containing process additive according to claim 1 wherein the first and second fluoropolymer components are each semi-crystalline and the melt point of the second component is higher than the melt point of the first component.
- 20 4. A co-coagulated fluorine-containing process additive according to claim 2 wherein the first and second fluoropolymer components are each semi-crystalline and the melt point of the second component is higher than the melt point of the first component.
- 25 5. A co-coagulated fluorine-containing process additive according to claim 3 wherein the first and second fluoropolymer components are each semi-crystalline and the melt point of the first component is less than 150° C.
- 30 6. A co-coagulated fluorine-containing process additive according to claim 4 wherein the first and second fluoropolymer components are each semi-crystalline and the melt point of the first component is less than 150° C.

7. A co-coagulated fluorine-containing process additive according to claim 3 wherein the melt point of the second component is at least 10° C higher than the melt point of the first component.
- 5 8. A co-coagulated fluorine-containing process additive according to claim 4 wherein the melt point of the second component is at least 10° C higher than the melt point of the first component.
- 10 9. A co-coagulated fluorine-containing process additive according to claim 1 wherein the first fluoropolymer component comprises an amorphous fluoropolymer.
10. A co-coagulated fluorine-containing process additive according to claim 2 wherein the first fluoropolymer component comprises an amorphous fluoropolymer.
- 15 11. A method for improving the performance of the extrusion of a host polymer comprising the steps of,
- a. providing a coagulum of a simultaneously coagulated blend of latex particles comprising a first fluoropolymer component comprising (i) an amorphous fluoropolymer, (ii) a semicrystalline fluoropolymer or (iii) a blend thereof, and a second fluoropolymer component comprising a semicrystalline fluoropolymer, and
- 20 b. combining an effective amount of the coagulum with the host polymer, and
- c. extruding the combined product of step b.
- 25 12. A method according to claim 11 wherein the first fluoropolymer component comprises an amorphous fluoropolymer.
13. A method according to claim 11 wherein the fluoropolymer of the first fluoropolymer component comprises a semi-crystalline fluoropolymer and the melt point of the semi-crystalline fluoropolymer of the second component is higher than the melt point of the semi-crystalline fluoropolymer of the first component.
- 30

14. A method according to claim 13 wherein the melt point of the second component fluoropolymer is at least 10° C higher than the melt point of the first component fluoropolymer.

5 15. A method according to claim 13 wherein the combined product of host polymer and coagulum is processed at a processing temperature above the melt point of the first fluoropolymer component and below the melt point of the second fluoropolymer component.

10 16. A method for providing a fluorine-containing polymer process aid with improved flow properties comprising the steps of

- a. providing a first latex component comprising an amorphous fluoropolymer, a semi-crystalline fluoropolymer or blends thereof,
- b. providing a second latex component comprising a semi-crystalline
- 15 fluoropolymer,
- c. blending the first and second latex components to form a latex blend,
- d. simultaneously coagulating the latex blend to form a coagulum,
- e. separating the coagulum from the liquid of the latex blend, and
- f. optionally, reducing the particle size of the coagulum.

20

17. A method according to claim 16 wherein the first component comprises a semi-crystalline fluoropolymer with a melt point of less than 150° C and the melt point of the first fluoropolymer component is below the melt point of the second fluoropolymer component.

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18. A method according to claim 17 wherein the melt point of the fluoropolymer of the second component is 10° C or more above the semi-crystalline fluoropolymer of the first component.

30 19. A method according to claim 16 wherein the fluoropolymer of the first component comprises an amorphous fluoropolymer.

20. A shaped article made from a composition comprising a host polymer comprising a process aid produced as described in claim 11.

21. A method according to claim 11 wherein the ratio of the first component to the second component is from 30:70 to 80:20.

22. A method according to claim 21 wherein the ratio of the first component to the second component is preferably from 40:60 to 60:40.

23. A method according to claim 16 wherein the ratio of the first component to the second component is from 30:70 to 80:20.

24. A method according to claim 16 wherein the ratio of the first component to the second component is preferably from 40:60 to 60:40.

25. A shaped article made from a composition comprising a host polymer comprising a process aid as described in claim 1.

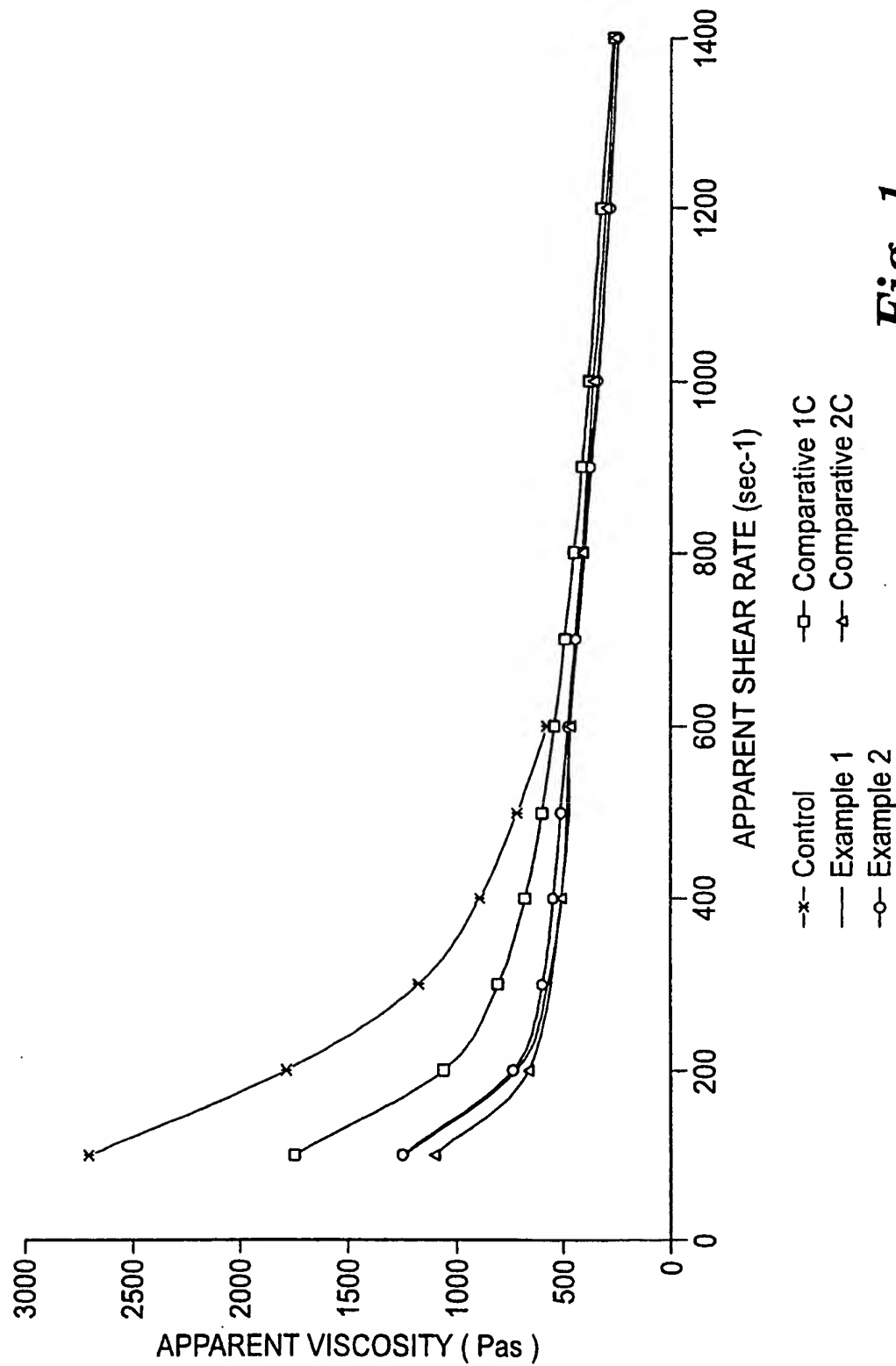
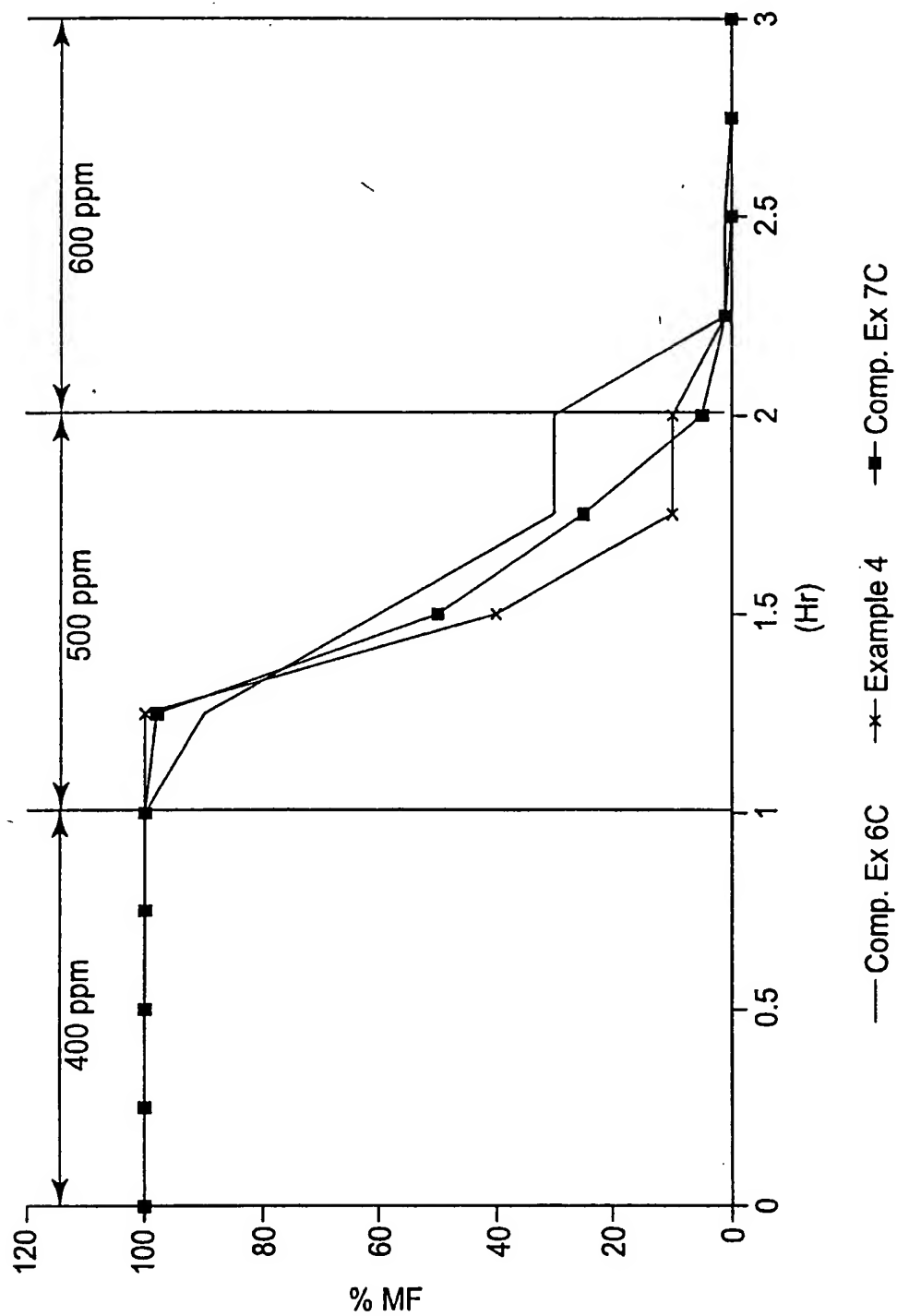
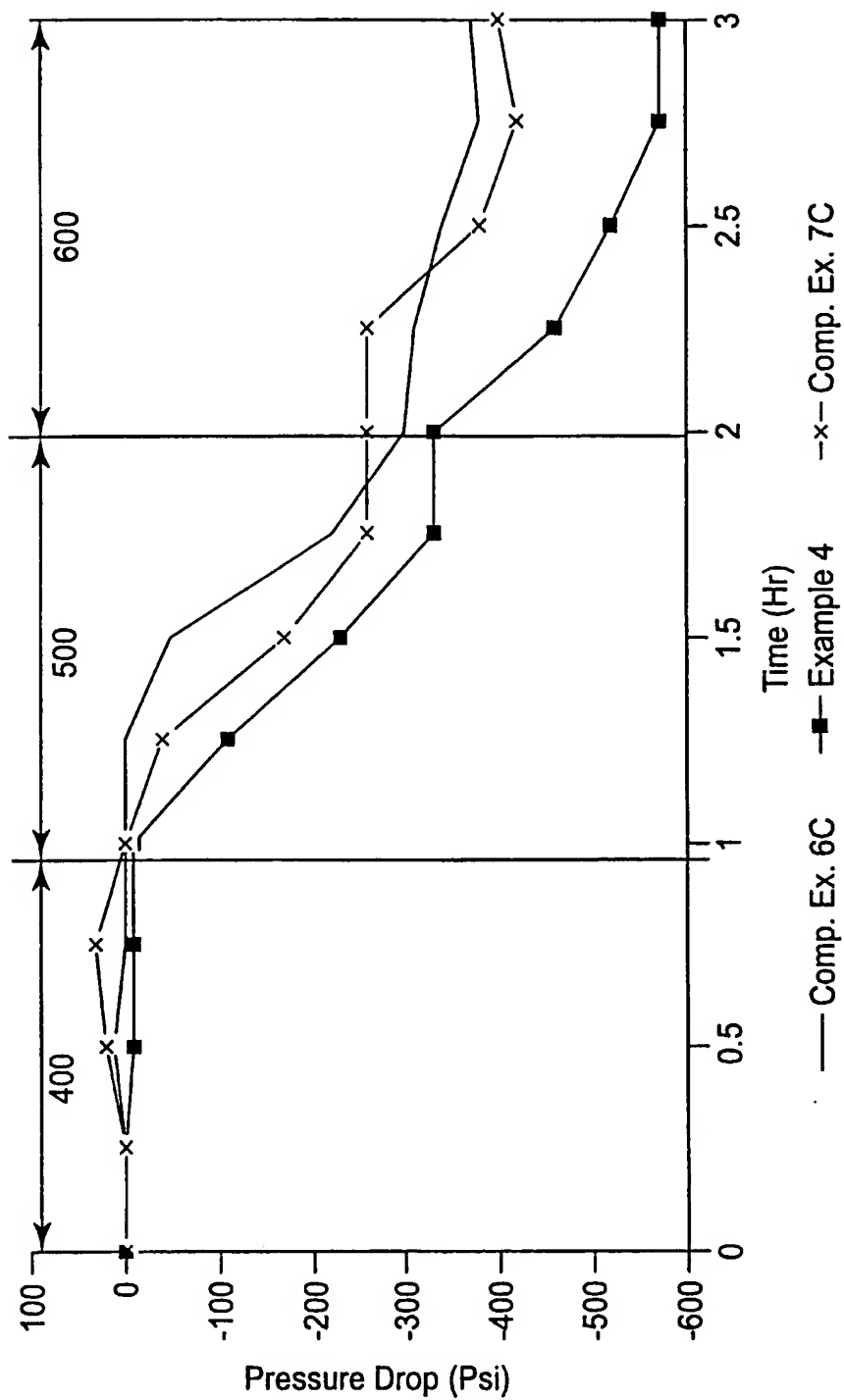


Fig. 1

**Fig. 2**

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**Fig. 3**

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/28088

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L27/12 C08L23/16 //(C08L27/12,27:12),(C08L23/16,27:12,27:12)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, CHEM ABS Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 798 854 A (VISCA MARIO ET AL) 17 January 1989 (1989-01-17)	1-10, 16-19
Y	claims; examples 5,8-10 ----	1-25
X	US 4 904 735 A (CHAPMAN JR GEORGE R ET AL) 27 February 1990 (1990-02-27)	20,25
Y	cited in the application claims; examples ----	1-25
A	US 5 106 911 A (CHAPMAN JR GEORGE R ET AL) 21 April 1992 (1992-04-21)	1-25
	claims; examples -----	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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G document member of the same patent family

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5 February 2001

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/28088

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4798854 A	17-01-1989	IT 1190352 B AU 5567686 A AU 594048 B CA 1279424 A DE 3688570 A DE 3688570 T EP 0202012 A ES 554180 D ES 8800302 A JP 6053808 B JP 62011731 A JP 62104871 A US 5115026 A	16-02-1988 09-10-1986 01-03-1990 22-01-1991 22-07-1993 23-09-1993 20-11-1986 01-11-1987 01-01-1988 20-07-1994 20-01-1987 15-05-1987 19-05-1992
US 4904735 A	27-02-1990	CA 1338727 A	19-11-1996
US 5106911 A	21-04-1992	AT 144271 T AU 622050 B AU 6419390 A BR 9006939 A CA 2027099 A DE 69028915 D DE 69028915 T EP 0447512 A JP 3505346 T KR 9506266 B WO 9105009 A	15-11-1996 26-03-1992 28-04-1991 17-12-1991 07-04-1991 21-11-1996 15-05-1997 25-09-1991 21-11-1991 13-06-1995 18-04-1991